

# Can hydrogen be stored inside carbon nanotubes under pressure in gigapascal range?

X. H. Zhang,<sup>1,2</sup> X. G. Gong,<sup>1</sup> and Z. F. Liu<sup>2</sup>

<sup>1</sup>*Department of Physics, Fudan University, Shanghai 200433, China*

<sup>2</sup>*Department of Chemistry, Chinese University of Hong Kong, Shatin, Hong Kong, China*

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By using a newly fitted multi-parameter potential to describe the van der Waals interaction between carbon and molecular hydrogen, we study the hydrogen storage inside carbon nanotubes (CNT's) under pressure in gigapascal range. Comparing with the results of graphite, we find that the shape change of the nanotubes (the curvature effect) provides a different storage mechanism for hydrogen. The negative free energy change for hydrogen storage inside CNT's makes it possible to use CNT's as the nanocontainer [Carbon **45**, 315 (2007)].

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## I. INTRODUCTION

Technologies using hydrogen as an energy source are being developed rapidly, among which the hydrogen storage in carbon materials is one major aspect.<sup>1</sup> Dillon *et al.*<sup>2</sup> are the first that suggested the possibility of achieving very high hydrogen storage capacity by using single-wall carbon nanotubes (SWCNT's). By experiments using high-purity SWCNT's, hydrogen storage capacity of about 8 wt% at 80 K and 120 atm was reported by Ye *et al.*,<sup>3</sup> and about 4.2 wt% at room temperature and 100 atm by Liu *et al.*<sup>4</sup> On the other hand, molecular dynamics simulations and the Monte Carlo method were used to study the hydrogen adsorption.<sup>5,6</sup> However, there are still many open questions to be resolved, for example, whether hydrogen is chemisorbed or physisorbed in carbon materials and whether the intratube space of SWCNT's is more important than the intertube space.

The report by Ma *et al.*<sup>7</sup> that chemisorption is achieved by collision of H atom with energy of 1-3 eV, and the report by Chan *et al.*<sup>8</sup> on the breaking of the H-H bond between carbon nanotubes under high pressure show the possibility of the chemisorption. Very recently, an experimental study should be a breakthrough for the chemisorption,<sup>9</sup> that carbon nanotube films are found to be hydrogenated and the C-H bonds can be broken by heating to 600°C.

However, for the much more widely studied physisorption, there are very few exciting results. In 2004, Chan *et al.*<sup>10</sup> found by *ab initio* calculation that H<sub>2</sub> molecules can be well confined between graphene sheets under pressure in the gigapascal range due to the negative free energy change  $\Delta G$ . This method is much better than many of the other simulations, because in those studies either the external pressure is not considered or the interaction between carbon atoms and H<sub>2</sub> molecules are not well described. For example, Ma and Xia *et al.*<sup>11,12,13</sup> studied the energy between H<sub>2</sub> molecules and the wall of the SWCNT and found helical structures of hydrogen inside the tube. However, we don't know whether the H<sub>2</sub> molecules want to stay inside the tube or not, because the tube in their studies is encapsulated. Furthermore

their potentials describing the C-H<sub>2</sub> and H<sub>2</sub>-H<sub>2</sub> interactions are both Lennard-Jones (LJ) like, which are not accurate under high pressure<sup>14,15</sup>.

In this study, by using molecular dynamics simulations with a more accurate multi-parameter potential for C-H<sub>2</sub> van der Waals (vdW) interaction,<sup>15</sup> we investigate the hydrogen storage inside the graphene sheets and carbon nanotubes under pressure. We find that the carbon nanotubes have a different storage mechanism from the graphite. For the graphite system, one must separate the graphene sheets by overcoming a large binding energy to store the H<sub>2</sub> molecules. But in the nanotubes, such binding energy is easy to overcome because the storage of hydrogen relaxes the tube from fully collapsed shape (thin ellipse) to fat ellipse and provides more negative contribution to the total energy change. This is the main reason that hydrogen storage inside nanotubes might has a negative free energy change which is the key criterion for the storage.

Furthermore, our research also shows the possibility of CNT-based nanocontainer,<sup>16</sup> in which the hydrogen can be filled inside the container under high pressure and can be locked inside the tube due to molecular valves located at the two ends of the tube.

## II. METHODOLOGY

*Energy changes* – To calculate the free energy change we simulate pure molecular hydrogen (H<sub>2</sub>), pure carbon system (C), and hydrogen-intercalated carbon system (C+H<sub>2</sub>), respectively. Thus the free energy change can be written as

$$\begin{aligned}\Delta G &= \Delta H - T\Delta S = \Delta E + p\Delta V - T\Delta S \\ &= \Delta E + p\Delta V - T(S(\text{C}+\text{H}_2) - [S(\text{C}) + S(\text{H}_2)]) \\ &\approx \Delta E + p\Delta V + TS(\text{H}_2).\end{aligned}\quad (1)$$

Here we consider the entropy difference between pure and hydrogen-intercalated carbon system as zero, because under high pressure, the H<sub>2</sub> molecules inside carbon systems are well confined to form an ordered structure.

In order to study the hydrogen storage mechanism, we also divide the energy into four parts,

$$(C+H_2): E = E_{CC}^1 + E_{CC}^2 + E_{H_2-H_2} + E_{C-H_2}, \quad (2)$$

$$(C): E = E_{CC}^1 + E_{CC}^2, \quad (3)$$

$$(H_2): E = E_{H_2-H_2}, \quad (4)$$

where  $E_{CC}^1$  and  $E_{CC}^2$  are the covalent and the vdW energy between carbon atoms respectively,  $E_{H_2-H_2}$  is the energy between  $H_2$  molecules, and  $E_{C-H_2}$  is the energy between carbon and molecular hydrogen. Thus  $\Delta E$  can be written in the form

$$\Delta E = \Delta E_{CC}^1 + \Delta E_{CC}^2 + \Delta E_{H_2-H_2} + E_{C-H_2}. \quad (5)$$

**Systems** – The cubic simulation cell for pure hydrogen contains 2400 molecules. For hydrogen storage inside graphite, we simulated one 1920-C graphite and  $N$ - $H_2$ -intercalated 960-C graphite where  $N = 480, 960$ , and 1440, respectively. Periodic boundary conditions are used in all three directions ( $x$ ,  $y$ , and  $z$ ) for above simulation cells.

For the tubes, one 600-C (15,15) SWCNT and one 400-C (10,10) SWCNT are chosen in our study. Inside the tubes, we put different number of hydrogen, such as 150, 200, and 300  $H_2$  inside the (15,15) tube and 80, 100, and 150  $H_2$  inside the (10,10) tube. The nanotubes are periodic along their axial direction ( $z$ ).

**Simulation details** – The carbon atoms are coupled to a heat bath by using the Berendsen velocity scaling method,<sup>17</sup> while all  $H_2$  molecules inside the carbon systems are free. Simulations show the carbon atoms maintain at the set temperature 300 K with reasonably small fluctuations and the  $H_2$  molecules can reach such temperature in picoseconds. For pure hydrogen, the temperature is controlled by the same method.

For each direction with periodic boundary condition, the external pressure is applied using the Berendsen algorithm,<sup>17</sup> while for the  $xy$  plane of the carbon nanotubes, a constant-pressure method for finite systems is used.<sup>18</sup> We also use another method to apply the hydrostatic pressure on the tube in the  $xy$  plane, by introducing quite a large number of inert gas (He) to transmit the pressure. These two methods produce the same results. However, the latter method is the real way to apply the pressure in experiments.

The velocity verlet method is used to resolve the motion equation, with the time step 1.0 fs. After the system reaches the equilibrium, all data are got by averaging in 50 ps.

**Empirical potentials** – At temperature of 300 K and moderate pressure range,  $H_2$  molecules can be treated as structureless spherical particles, and are modeled by the Silvera-Goldman potential.<sup>14</sup> The C-C covalent bonds in graphite and carbon nanotubes are described by using the Brenner potential,<sup>19</sup> which has been widely used for carbon systems. For the C-C vdW interactions, a conventional treatment of LJ potential,  $V = C_{12}/r^{12} - C_6/r^6$ ,

TABLE I: Fitted parameters for the multi-parameter C- $H_2$  potential.

Parameter	Value	Parameter	Value
$\alpha$	1.55888	$C_6$	15.978 eV $\text{\AA}^6$
$\beta$	0	$C_8$	0 eV $\text{\AA}^8$
$\gamma$	0.642395	$C_{10}$	1166.92 eV $\text{\AA}^{10}$
$r_m$	6.21452	$\text{\AA}$	

where  $C_{12} = 2.48 \times 10^4$  eV $\text{\AA}^{12}$  and  $C_6 = 20$  eV $\text{\AA}^6$ , is adopted. By using such potential, at 300 K and zero pressure, the binding energy for two graphene sheets is 30.7 meV/atom with interplanar spacing of 3.30  $\text{\AA}$ , which is in agreement with both experimental and the density functional theory results those range from 25 to 57 meV/atom with the same spacing.<sup>20</sup> For the C- $H_2$  vdW interactions, we use a more accurate multi-parameter potential,<sup>15</sup>

$$\phi(r) = \exp(\alpha - \beta r - \gamma r^2) - \left( \frac{C_6}{r^6} + \frac{C_8}{r^8} + \frac{C_{10}}{r^{10}} \right) \times \exp \left[ - \left( \frac{r_m}{r} - 1 \right)^2 \right], \quad (6)$$

which is fitted from *ab initio* results and can provide a good description for high pressure regimes. The parameters for this potential are listed in Table I.

### III. HYDROGEN INSIDE GRAPHITE

**Layered structure** – We plot the hydrogen structure between two graphene sheets in Figure 1. Layered structure is formed under high pressure with the number of layer dependent on the molecule number. The top view [Figure 1(d)] shows all the  $H_2$  molecules are well confined between the hexagonal rings of the graphene sheets, in agreement with the Sandwich structure in Chan *et al.*'s study.<sup>10</sup> Figure 1(e) shows the trajectory of one  $H_2$  molecule in the three-layered structure under 5.0 GPa. The molecule hops from one confined position to another in about 10 ps after the external pressure increases, and stays for ever. Different from the liquid state under the same pressure, the hydrogen is a solid because such hopping phenomenon is very few and can not be found any more under higher pressure. This is interesting because at room temperature the pure hydrogen becomes solid under a higher pressure about 8.9 GPa.<sup>21</sup>

Simulations also show the hydrogen inside the graphite reaches this layered structure through two-step condensations. For example, in the graphite system with the number ratio of C: $H_2$ =2:1, the gas hydrogen undergoes the first condensation to form a two-layered structure under pressure about 0.5 GPa. With increasing the pressure, the hydrogen becomes more liquid-like. The second condensation happens under  $\sim 2.0$  GPa to form a one-layered solid-like structure. For the number ratio of 1:1 and 2:3, the pressures for the second condensation are 3.7 and 4.6 GPa, respectively.

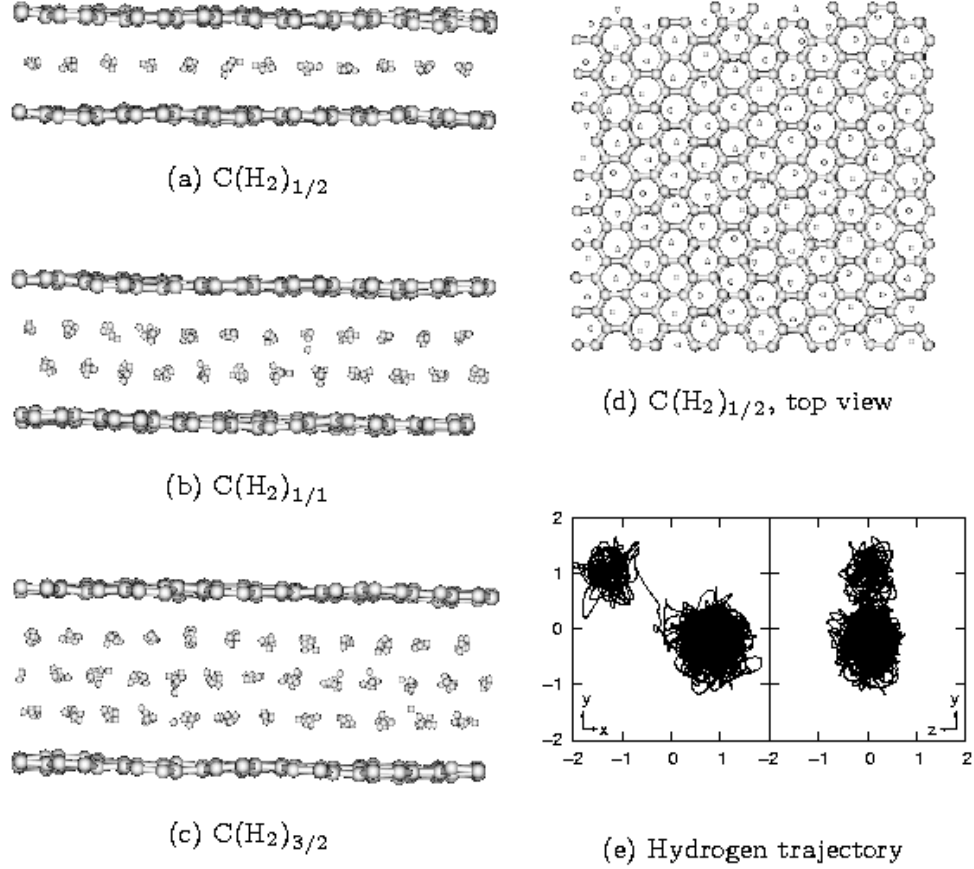


FIG. 1: Hydrogen structure between graphene sheets under 6.0 GPa at 300 K. (a)-(c): different layers for different number of hydrogen; (d): a top view for the (a) structure; (e): the trajectory of one  $H_2$  molecule for the (c) structure under 5.0 GPa. The trajectory shows that the molecule hops from one confined position to another and stays there for ever. Such hopping phenomenon just happens under low pressure and at the time when the pressure increases. The length unit for the trajectory is angstrom ( $\text{\AA}$ ).

In Figure 2 we show the hydrogen volume (right) and the pressure of hydrogen along the  $xy$  plane (left).

**Energy changes** – Table II shows the energy changes calculated using Equation 1 and 5. The positive free energy changes here are different from the *ab initio* study,<sup>10</sup> mainly because of the different  $p\Delta V$  values. Our studies show a negative  $p\Delta V$  when the pressure is smaller than 5.8 GPa, in agreement with the *ab initio* study. However, the values are different. For example, under 2.0 GPa the  $p\Delta V$  term for  $C(H_2)_{1/2}$  of -0.0146 eV per  $H_2$  molecule is much smaller than the *ab initio* result of -0.0975 eV. The reason is easy to find out that in the *ab initio* study, the supercell contains only 8  $H_2$  molecules that even under small pressure the hydrogen is fully confined.

We also provide the contributions to the total energy change  $\Delta E$  to analysis the storage mechanism. One can find from the table that  $\Delta E_{CC}^1$  is nearly zero. This

is because the graphene sheets keep their plane structure all the time, without changing the covalent energy. The positive  $\Delta E_{CC}^2$  terms show that the storage process should overcome the binding energy between graphene sheets. Fortunately, the negative  $E_{C-H_2}$  is almost in the same magnitude as  $\Delta E_{CC}^2$ . The cancellation between these terms makes only  $\Delta E_{H_2-H_2}$  left to the total energy change.  $\Delta E_{H_2-H_2}$  becomes more negative with increasing the pressure is because the hydrogen inside graphite is solid and can not be further compressed along the two directions ( $x$  and  $y$ ) of the graphene plane due to the graphene's hexagonal structure, while the pure hydrogen can be compressed further in all three directions.

In all three simulations,  $\Delta E$  are negative beyond few GPa. However, the magnitudes of  $\Delta E$  and  $p\Delta V$  are so small that they can not overcome the quite large  $T\Delta S$  term. In other words, such layered structure under high

TABLE II: Energy changes per hydrogen molecule for pressures under which hydrogen is fully confined between graphene sheets. All three simulations for different carbon-hydrogen number ratios show positive free energy change  $\Delta G$ , which becomes more positive with increasing the number of hydrogen. Specially for the number ratio of C:H<sub>2</sub>=2:1,  $p\Delta V$ ,  $T\Delta S$ , and the contributions to the total energy change  $\Delta E$  are provided.

Pressure (GPa)	$\Delta G$ for C(H <sub>2</sub> ) <sub>x</sub>			$\Delta E$ for C(H <sub>2</sub> ) <sub>1/2</sub>					$p\Delta V$ for C(H <sub>2</sub> ) <sub>1/2</sub>	
	$x = 1/2$	$x = 1/1$	$x = 3/2$	$\Delta E_{CC}^1$	$\Delta E_{CC}^2$	$\Delta E_{H_2-H_2}$	$E_{C-H_2}$	$\Delta E$		$T\Delta S$
4.5	0.0939	0.1134	0.1338	0.0006	0.1026	-0.0279	-0.0965	-0.0211	-0.0137	0.1287
5.0	0.0820	0.1050	0.1118	0.0010	0.1000	-0.0455	-0.0903	-0.0347	-0.0088	0.1256
5.5	0.0717	0.0948	0.1020	0.0012	0.0975	-0.0617	-0.0839	-0.0468	-0.0037	0.1222
6.0	0.0619	0.0858	0.0935	0.0014	0.0949	-0.0776	-0.0769	-0.0583	0.0017	0.1185
6.5	0.0522	0.0772	0.0854	0.0018	0.0923	-0.0936	-0.0700	-0.0695	0.0071	0.1146
7.0	0.0419	0.0687	0.0766	0.0021	0.0895	-0.1095	-0.0629	-0.0808	0.0121	0.1106

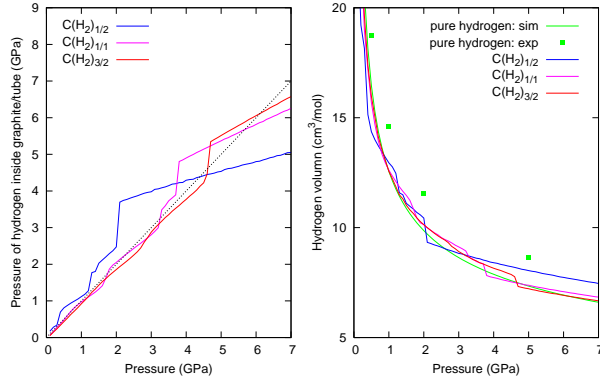


FIG. 2: The pressure (left) and the volume (right) of the hydrogen between graphene sheets. Green squares are taken from the experimental data<sup>21</sup> and the others are the results in our simulations.

pressure is energetically favorable but not allowed due to the positive free energy change.

**Pressure of hydrogen** – We also calculate the pressure of hydrogen between the graphene sheets, as shown in Figure 2. Though the pressure of hydrogen inside is smaller than the external pressure, more hydrogen intercalation is not allowed because of the positive  $\Delta G$ . Negative  $\Delta G$  is the first rule for hydrogen storage, then the pressure is another judgment that at the maximum storage the pressure of hydrogen is no larger than the external one.

#### IV. HYDROGEN INSIDE CARBON NANOTUBES

**Hydrogen structure** – Figure 3 shows the layered structure of hydrogen inside the (15,15) CNT under high pressure. The hydrogen-intercalated system also undergoes step-by-step hydrogen condensations to reach the final layered hydrogen structure, similar to hydrogen inside the graphite. For the number ratio of C:H<sub>2</sub>=4:1, there is another phase transition under pressure about 6.1 GPa,

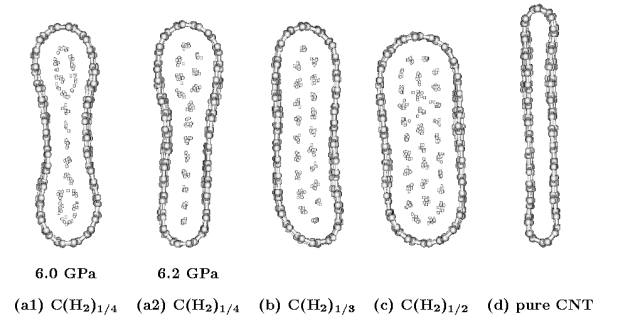


FIG. 3: Hydrogen structure inside (15,15) CNT under 6.0 GPa at 300 K. Specially for the number ratio of C:H<sub>2</sub>=4:1, there is a phase transition under 6.1 GPa, with different structures before (6.0 GPa) and after (6.2 GPa) the transition shown in (a1) and (a2). In order to show the curvature effect, the structure of pure CNT under 6.0 GPa is also shown.

that before the transition only the middle part of the hydrogen is well confined while after the transition the hydrogen show one-layered structure in one part and two-layered in another. These structures are shown in Figure 3(a1) and Figure 3(a2), respectively. For the H<sub>2</sub> molecules, the main difference from the hydrogen inside graphite is the molecules at the two ends of the ellipse have more carbon neighbors and therefore have lower energy than other H<sub>2</sub> molecules in the middle of the ellipse.

On the other hand and more important, with hydrogen intercalation, the CNT wall relaxes itself to release its elastic energy. One can find the different bent shapes for the tube with and without hydrogen inside from Figure 3. For the pure carbon CNT under pressure, the shape of the cross section is an elongated ellipse, with a large elastic energy at the two ends of the ellipse. But when the hydrogen is intercalated, the curvature becomes larger at the two ends. Such effect is new for CNT's, and will contribute more negative energy change for hydrogen storage.

**Energy changes** – As we expected, hydrogen storage

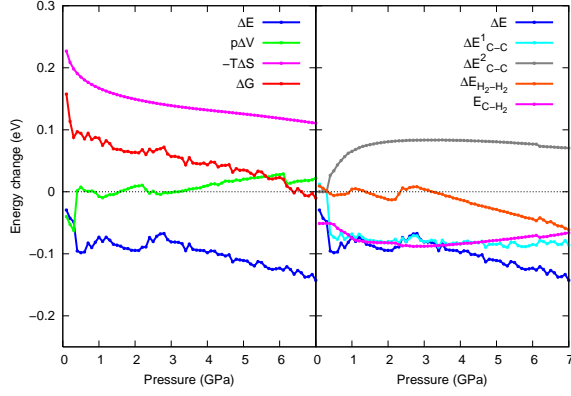


FIG. 4: Energy changes for (15,15) CNT:  $C(H_2)_{1/4}$ . There are several jumps in the energy changes, corresponding to different phase transitions or hydrogen condensations: (i) the phase transition of pure (15,15) CNT (0.3 GPa), (ii) the first hydrogen condensation (0.9-1.1 GPa), (iii) the second hydrogen condensation (2.2-2.4 GPa), and (iv) the final phase transition of hydrogen to form a well confined structure (6.1 GPa), as described in the text.

inside CNT's produces more negative  $\Delta E$ . Fortunately, the magnitude of  $p\Delta V$  is still quite small despite of the sign, thus the free energy change  $\Delta G$  might be negative under pressure. Figure 4 shows the energy changes for hydrogen inside (15,15) CNT with the number ratio of  $C:H_2=4:1$ .<sup>22</sup> It is quite interesting to find that under pressure above 6.4 GPa,  $\Delta G$  is negative (-0.0016 and -0.0101 eV per  $H_2$  molecule for 6.4 and 7.0 GPa respectively). For the number ratio of 3:1,  $\Delta G$  is also negative under 7.0 GPa (-0.0011 eV).

Considering that in the  $\Delta G$  calculation the entropy difference between the pure and hydrogen intercalated carbon system is taken to zero, the real  $\Delta G$  should be a little smaller, or in other words, more negative. This result is quite different from the graphite that under pressure in gigapascal range, hydrogen storage inside carbon nanotube is free-energetically favorable.

When more and more hydrogen ( $C:H_2=2:1$ ) is inside the tube, we find  $\Delta G$  increases to 0.0187 eV per  $H_2$  molecule even under 7.0 GPa. It shows the maximum storage of hydrogen in our pressure range is between the number ratio of  $C:H_2=3:1$  and  $2:1$ .

To find out the reason why hydrogen can be stored in CNT, we still should look into the contributions to the total energy change  $\Delta E$ . In Figure 4 one can find that the covalent bonding energy between carbon atoms contributes now, shown in the  $\Delta E_{CC}^1$  term, as we have explained above. Hydrogen inside the tube relaxes the tube wall and cause a negative energy change, which cancels the positive vdW binding energy change  $\Delta E_{CC}^2$ . We will show that  $\Delta E_{CC}^1$  can be more negative when the tube radius decreases. However, for the left two contributions  $\Delta E_{H_2-H_2}$  and  $E_{C-H_2}$ , they are still as the same as those in graphite. In all, due to the curvature effect, hydrogen storage inside CNT causes  $\Delta E_{CC}^1$  to be negative and

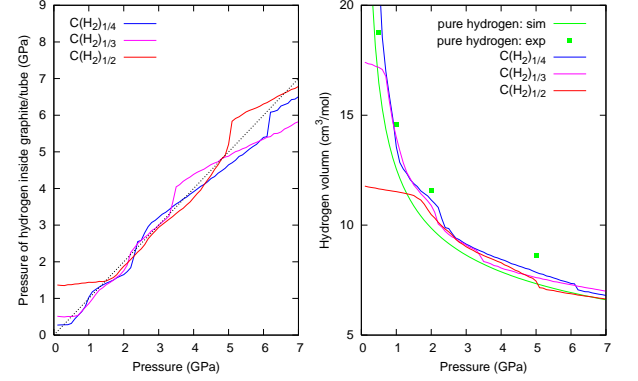


FIG. 5: Hydrogen pressure for the storage inside (15,15) CNT along the direction ( $z$ ) of the tube axis (left) and the volume of the hydrogen, similar to Figure 2.

makes the total energy change  $\Delta E$  large enough to overcome the  $T\Delta S$  term.

**Pressure of hydrogen** – In Figure 5 we show the calculation of the hydrogen pressure along the tube axis direction ( $z$ ) and the volume for the hydrogen. We can also get the maximum storage capacity for (15,15) CNT from the figure. For the number ratio of  $C:H_2=4:1$  and  $3:1$ ,  $\Delta G$  is negative under  $\sim 7.0$  GPa. At the same time, the pressure inside is smaller than the external one, thus more hydrogen can be stored due to the negative free energy change.

TABLE III:  $\Delta G$  for (10,10) and (15,15) CNT.  $x$  is the number ratio between molecular hydrogen and carbon atoms, labeled by  $C(H_2)_x$ . The unit for  $\Delta G$  is eV per  $H_2$  molecule.

Pressure (GPa)	$\Delta G$ for (10,10) CNT			$\Delta G$ for (15,15) CNT		
	$x = 1/5$	$1/4$	$3/8$	$x = 1/4$	$1/3$	$1/2$
0.6	0.0164					
0.7	-0.0063	0.0209				
0.8	-0.0204	0.0676				
0.9	-0.0414	-0.0048				
1.0		-0.0194				
3.8			0.0006			
3.9			0.0020			
4.0			-0.0001			
4.1			-0.0058			
6.3				0.0050		
6.4				-0.0016		
6.5				0.0051		
6.6				0.0004		
6.7				-0.0060	0.0005	0.0211
6.8				-0.0067	0.0009	0.0204
6.9				-0.0026	0.0022	0.0220
7.0				-0.0101	-0.0011	0.0187

*Smaller tube* – When the radius of CNT decreases, the curvature plays more important role to the energy change. In our simulations for (10,10) CNT, we find that  $\Delta G$  is negative even under  $<1.0$  GPa, much smaller than the critical pressure for (15,15) CNT. Table III also shows that the critical pressure for a negative  $\Delta G$  increases with increasing the number of hydrogen.

## V. CONCLUSION

In summary, we have studied the hydrogen storage inside graphite and carbon nanotubes. Three results are listed below:

i) Hydrogen can not be stored inside graphite due to the positive energy change. The main reason is that the binding energy between graphene sheets is overcome only by the C-H<sub>2</sub> vdW interaction and the H<sub>2</sub>-H<sub>2</sub> energy change. So the total energy change  $\Delta E$  is not large enough to overcome the positive  $T\Delta S$  term. The hydrogen inside graphite is solid with hcp structure, and has a smaller internal pressure than the external one.

2) For the carbon nanotube, the hydrogen storage under pressure will relax the tube wall and bring an additional contribution to the total energy change. So it is possible to achieve a negative free energy change. For

example, under  $\sim 7.0$  GPa, hydrogen can be stored inside (15,15) CNT due to the negative free energy change, with the storage capacity higher than 5.2 wt%.

3) When the tube radius decreases, the curvature effect plays more important role in the total energy change. The negative free energy change can be achieved even under a small pressure.

Our results also show the possibility to design the CNT-based nanocontainer.<sup>16</sup> The hydrogen can be filled inside the tube under pressure in gigapascal range, and because of the molecular valves, when we unload the external pressure, molecular hydrogen will be locked inside the tube. Such fill-and-lock mechanism has been discussed by Ye *et al.*,<sup>16</sup> and is proved applicable by current studies.

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